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14. ABSTRACT We explore a new process for the formation of peptide nanotubes (PNTs) using plasma-enhanced chemical vapor deposition (PECVD). This state-of-the-art process allows coating of substrates with various peptides, while controlling the uniformity of the coating regardless of the substrate and with lower costs. In this study, a custom-built PECVD chamber (housed at AFRL/RX) has been modified to allow for the sublimation of solid monomers into the plasma stream and coat a variety of substrates held downstream from the plasma zone. The project was carried out in two stages; the first stage tested the feasibility of depositing diphenylalanine PNTs on activated carbon electrodes using PECVD in collaboration with AFRL. The second stage tested the quality of the deposited nanotubes and its effect on electrical capacitance and the contribution to the transfer of electrical cargo on activated carbon electrodes. Herein, we have demonstrated that surfaces such as activated carbon (both rough and smooth) can be coated with a layer of diphenylalanine peptide nanostructures. Coating rough carbon surfaces with peptides nanotubes can be inhomogeneous, but when these surfaces are treated with nitric acid, prior to the application of the peptides, the peptide coatings rearranged in homogenous forms of wires and tubes on the surface.						
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Plasma-Enhanced Chemical Vapor Deposition as a Method for the Deposition of Peptide Nanotubes

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Introduction:

The unique ability of dipeptides such as diphenylalanine (FF) to undergo self-assembly due to sublimation, has been exploited for the formation of vertically aligned nanotubes arrays.¹ Using physical vapor deposition (PVD) well-ordered assemblies of peptide nanotubes (PNTs) composed of dipeptide subunits are obtained on various surfaces (Figure 1a). . The deposition of the nanotubes occurs under vacuum and provides control over the length of the tubes, their density and the coverage extant of the peptide nanotubes layer. This array of PNTs has remarkable stability under various mechanical and chemical conditions.²⁻⁴

In our present study, we explore a new process for the formation of PNTs using plasma-enhanced chemical vapor deposition (PECVD)⁵. This state of the art process, allows coating of substrates with various peptides, while controlling the uniformity of the coating regardless of the substrate and with lower costs. PECVD is a form of chemical vapor deposition where inert gas plasma is used to enhance reactivity of organic/inorganic chemical species for the deposition of thin films (Figure 1b).

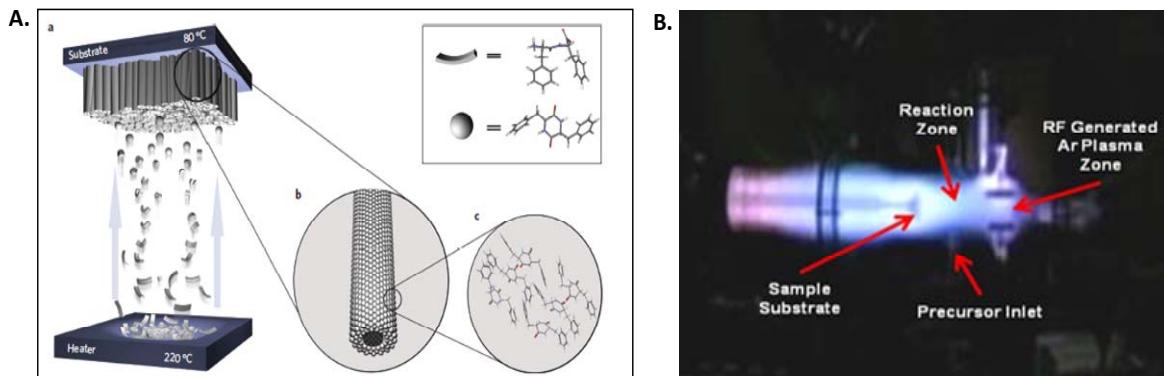


Figure 1. (a) Illustration of physical vapor deposition (PVD) process of diphenylalanine peptide into nanotubes¹ (b) The plasma enhanced chemical vapor deposition PECVD system.⁵

The use of plasma in order to coat surfaces is a well-established method, and is used to evaporate inorganic materials and metals with high vaporization pressures. Cold plasma used in the PECVD process allows control over the composition of the processed films

imparting unique surface properties without modifying the bulk material properties of the substrate. PECVD is a process used for the deposition of thin films during which the plasma generally breaks down the monomer, and then the monomer polymerizes on the substrate. The substrates can either be placed on the lower electrodes or downstream from the plasma to avoid plasma bombardment effects (as in this case). In this study, a home-built PECVD chamber (housed at AFRL/RX) has been modified to allow for the sublimation of solid monomers into the plasma stream and coat a variety of substrates held downstream from the plasma zone. A radio frequency (RF) electrode at 13.56 MHz has been used for the plasma generation process and a matching box was used in order to minimize reflected power. Inert gases such as argon were used for the plasma generation process.. The power supply can be continuous or pulsed with varying frequencies and duty cycles.

Results

The project was carried out in two stages; the first stage tested the feasibility of depositing diphenylalanine PNTs on activated carbon electrodes using PECVD in collaboration with AFRL. The second stage tested the quality of the deposited nanotubes and its effect on electrical capacitance and the contribution to the transfer of electrical cargo on activated carbon electrodes.

A. Deposition of Peptide Nanotubes using PECVD

First, we studied the feasibility of using PECVD for deposition of diphenylalanine -PNTs on silicon substrates. The monomers used for the sublimation were the L- and D-Diphenylalanine obtained from Bachem (Switzerland). The process was carried out using the PECVD deposition chamber with sublimation capability in the laboratory of Dr. Rajesh Naik (AFRL/RXAS) and conditions were modified for dipeptide deposition. While experimenting with different deposition conditions, it was found that heating the peptide to 200 °C was necessary in order to grow the peptides nanotubes on a substrate in the evaporator. It was observed that the peptides sublime and further undergo recrystallization on the cold substrate. The conditions in the plasma deposition process allows control on the morphology of the deposited PNTs. The deposited substrates were

then analyzed by scanning electron microscopy [SEM]. Figures 2-4 present the ability of the PECVD process to form a uniform layer of diphenylalanine PNTs over different surfaces. It can be seen that the coating can be applied on smooth surfaces such as silicon, and it is also possible to make patterned coatings (Figure 2).

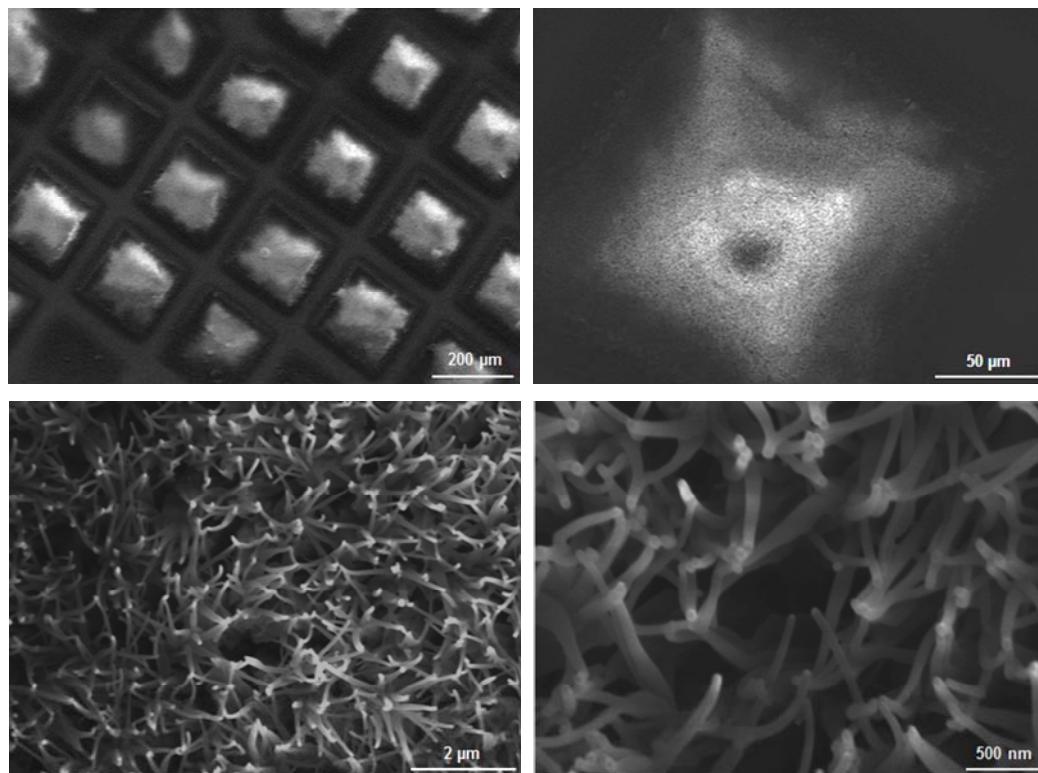


Figure 2. SEM images of patterned array of D-Diphenylalanine peptide assemblies deposited by PECVD process on silicon. Deposition duration was 3 min, with RF Power 30W (Frequency 100 Hz and duty cycle of 25%) and the peptide monomer was heated to 200°C. The height of the nanotubes was ~50 μm and the diameter was 85-100 nm.

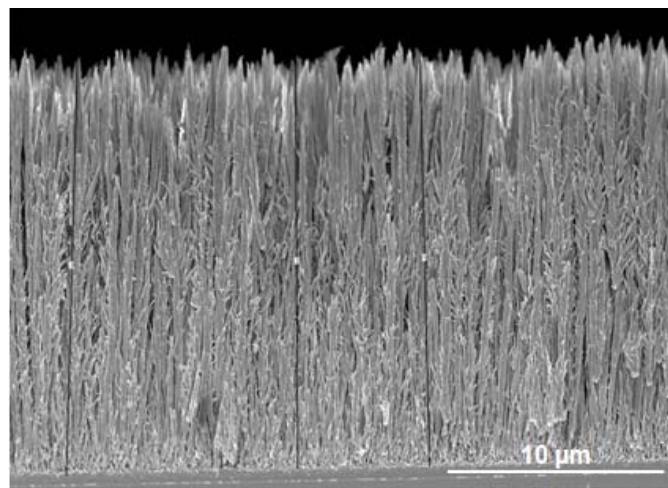


Figure 3: Cross-sectional SEM image of D-Diphenylalanine PNT assemblies deposited by PECVD process on silicon. Deposition duration was 3 min, with RF Power 30W (Frequency 250 Hz and duty cycle of 25%) and the sample was heated to 200°C. The height of the nanotubes was ~20 μm.

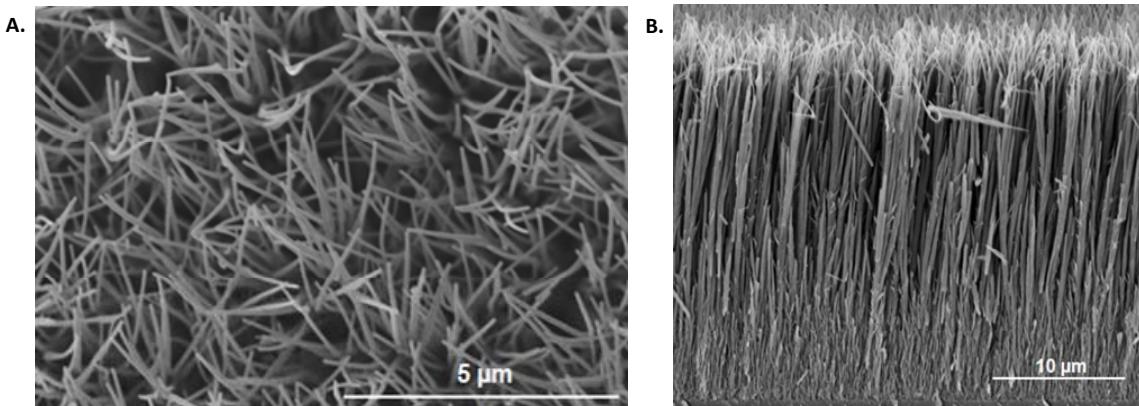


Figure 4. SEM images of L-Diphenylalanine PNT assemblies deposited by PECVD process on silicon. RF Power is 30W (continuous), the sample was heated to 200°C.

B. Diphenylalanine PNTs deposited on activated carbon electrode substrates via PECVD

To assess the quality of the deposited PNT, we plan to test the effect of different electrolytes on the electrical capacitance of carbon electrodes coated with a uniform layer of PNT deposited using PECVD process. For this purpose, activated carbon electrodes

were prepared, the carbon with micro perforations was glued with 20% polyvinylidene difluoride (PVDF) dissolved in N-Methyl-2-pyrrolidone (NMP) and flattened over graphite paper, so a uniform layer of activated carbon with a thickness of 100 microns was received (Figure 5). Some samples were further treated with concentrated nitric acid [HNO_3]. Figure 6 shows examples of SEM micrograph of the untreated activated carbon electrodes coated with PNT, and Figure 7 shows SEM micrograph of carbon electrodes after treatment with nitric acid. SEM images of the surfaces show that they were covered unevenly resulting from the non-uniformity of the activated carbon surface. However, samples that undergone nitric acid treatment prior to coating were coated evenly. Moreover, the diphenylalanine assemblies on both, the activated and non-activated carbon, exhibited similar morphology of mixed wires and tubes. Therefore, we can conclude that the activation process did not affect the nanostructure assembly.

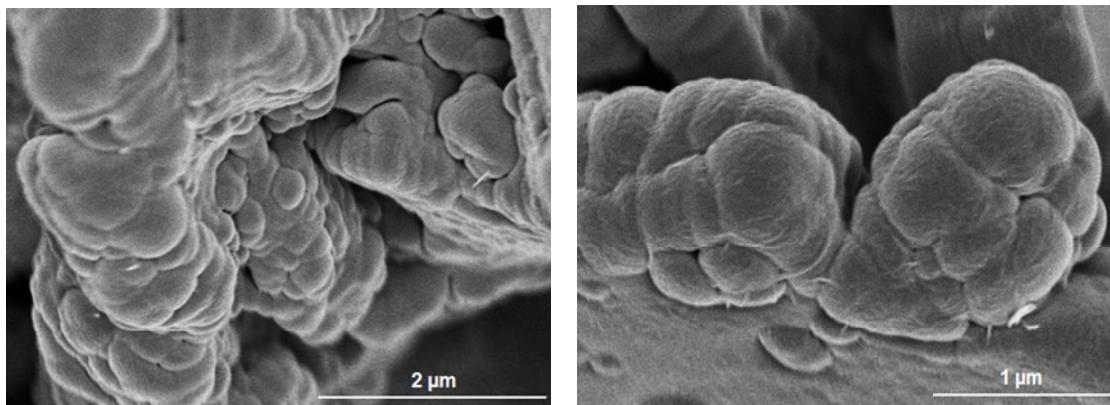


Figure 5. SEM images of activated carbon, following HNO_3 activation and exposure to plasma in the PECVD chamber shows that both exposure to HNO_3 and plasma does not affect the morphology of the activated carbon surface.

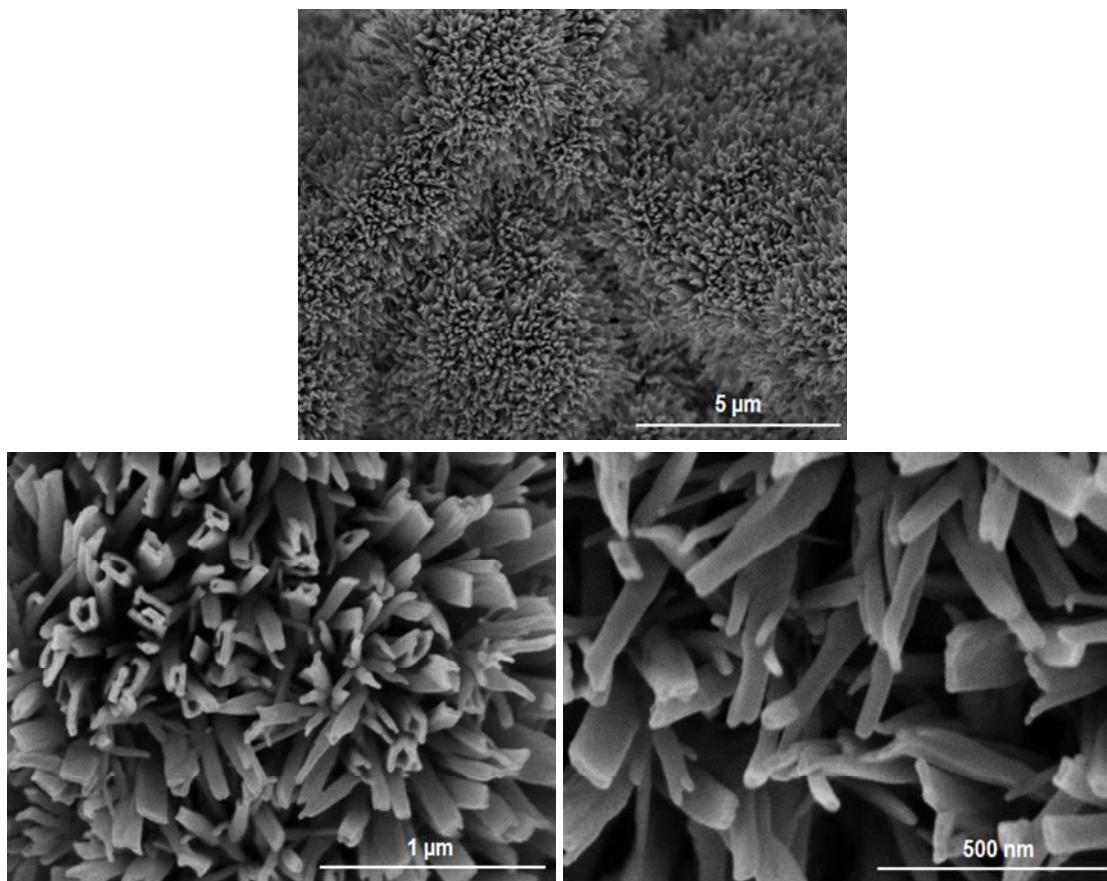


Figure 6: SEM images of L-Diphenylalanine PNTs deposited by PECVD process on pristine activated carbon substrates resulting in the formation of ordered elongated assemblies.

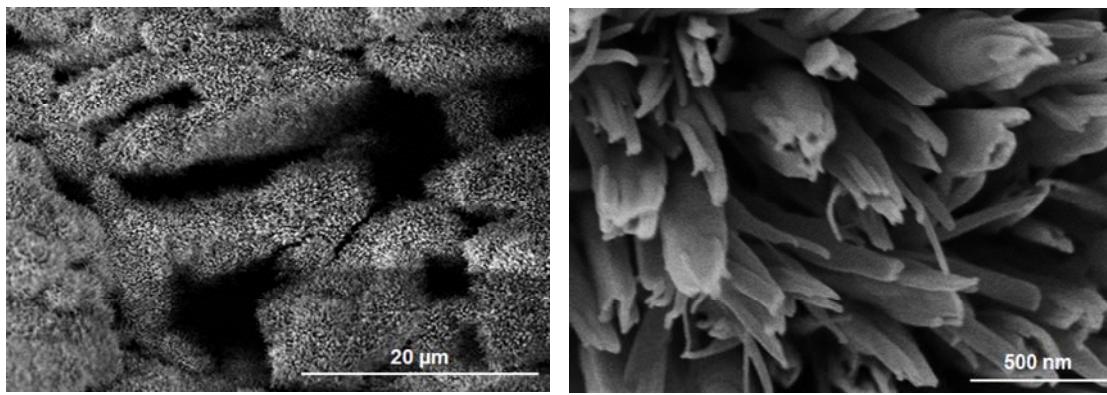


Figure 7: SEM images of D-Diphenylalanine PNTs deposited by PECVD process on activated carbon treated with HNO_3 , resulting in the formation of ordered elongated assemblies.

C. Electrochemical measurements

PNTs have been self-assembled from diphenylalanine peptide subunits. These nanotubes contain acidic groups, amine groups and amide connections between the two phenylalanine molecules (Figure 8). These groups are affected by varying pH and behave differently depending on the environment. Therefore, the capacitance measurements were done in two environments, in neutral and in acidic medium. These electrolytes help us evaluate the quality of the deposited PNT and the capability of the PNT layer to donate electrons. Measuring the capacitance in these two electrolytes allows us to test the activation and the influence of the PNT layer in the best way.

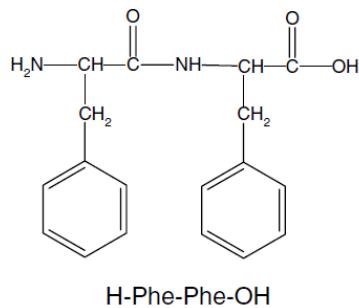


Figure 8. Scheme of L-Diphenylalanine peptide

We can see in figure 10 the behavior of the active carbon in neutral medium and in acidic medium (0.1M H₂SO₄, 0.1M KCl). The electrochemical window gets bigger (a wider voltammetric cycle is obtained when the capacity gets larger) and we get larger capacity with the activation in HNO₃. Electrochemical analysis of the samples in different electrolytes, acidic and neutral, shows that a larger capacity is obtained in the acidic medium, because of the higher conductivity of the acid. In acidic activated carbon, we received the largest capacity, because the acidic activation leaves more acidic surface groups which show higher activity in acidic medium due to specific adsorption of protons on the surface groups.

Conclusions:

Herein, we have demonstrated that surfaces such as activated carbon, (both rough and smooth) can be coated with a layer of diphenylalanine peptide nanostructures. Coating rough carbon surfaces with peptides nanotubes can be inhomogeneous, but when these surfaces are treated with nitric acid, prior to the application of the peptides, the peptide coatings rearranged in homogenous forms of wires and tubes on the surface.

Electrochemical measurements showed that the PNT coating increased the capacity by 10% in neutral electrolyte ($\text{pH}=7$), and by 28% in an acidic electrolyte. These results are for non-activated carbon electrodes only. Moreover, in the case on activated carbon electrodes, it seems that the PNT layer blocks the pathway of protons into the pores of the carbon, and hence reduces the capacity of these electrodes. For future investigation of this phenomenon, the influence of different carbon materials with different pore sizes should be analyzed.

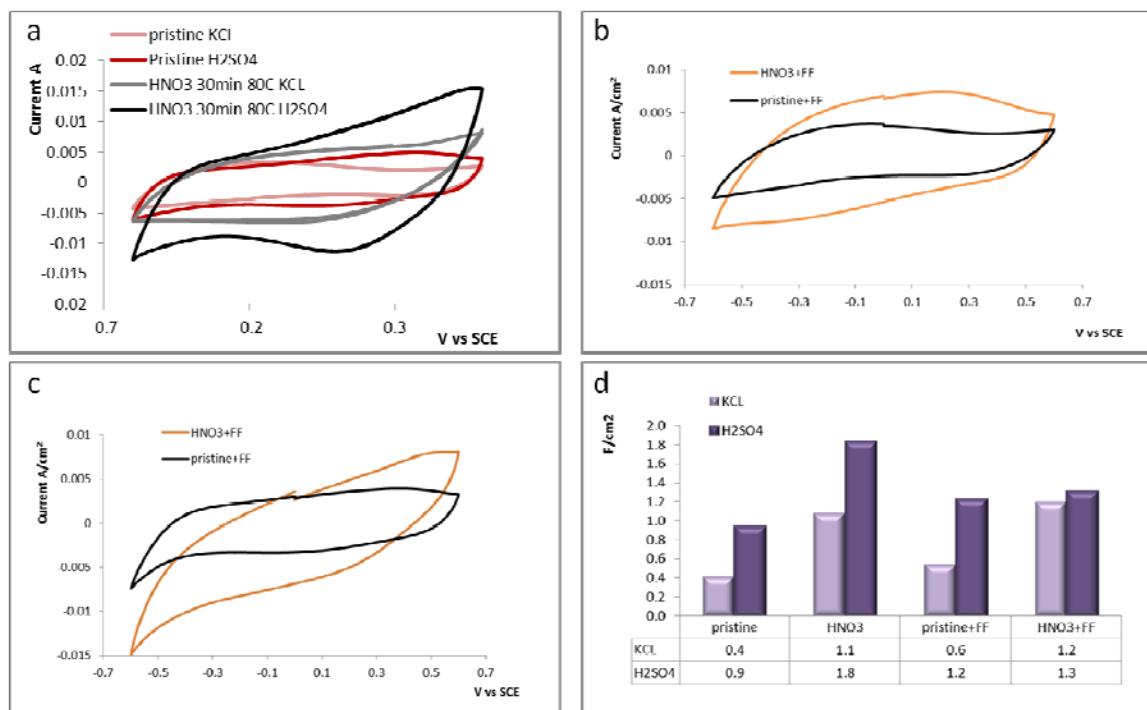


Figure 9. (a) Cyclic voltammetry [CV] analysis of activated carbon electrode with or without HNO_3 activation in neutral electrolyte KCl 0.1M or acidity electrolyte H_2SO_4 0.1M (surface of the electrode is 1 cm^2). (b) CV of activated carbon electrode with or

without HNO₃ activation coated with PNT in neutral electrolyte KCl 0.1M. (c) CV of activated carbon electrode with or without HNO₃ activation coated with PNT in acidity electrolyte H₂SO₄ 0.1M. (d) The calculated capacity at 0.1V of activated carbon with PNT deposit by PECVD.

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